Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings
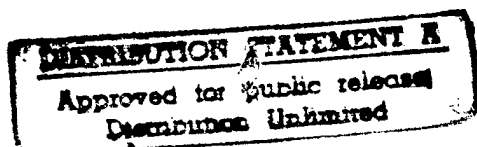
Quarterly Report # 2
December 19, 1996

for Dr. Harold Guard (ONR) and Dr. Thomas Moran (ARPA)
Contract #N00014-96--0147

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Title:	*Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings*
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Contract	N00014-96--0147
Project Officer:	Dr. Harold Guard ONR 331 Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217-5660

Proprietary Sections

The information contained on pages 5-16 is considered proprietary. TDA intends to file invention disclosures with the Office of Naval Research and also file patent applications for the technologies described on pages 5-16 when development of the alumoxane coatings are fully reduced to practice.

1. Project Objective

DoD organizations are large consumers of protective aircraft, vehicle, architectural, and industrial maintenance coatings. Because of the adverse operating conditions under which military aircraft and vehicles are called to operate, the coatings are usually replaced on a more frequent basis than coatings used in commercial applications. For the U.S. Air Force maintenance operations associated with stripping and re-coating aircraft and other painted surfaces amounts to $700 million per year. These maintenance operations also produce 70% of the Air Forces hazardous materials.

The Clean Air Act (CAA) of 1990 effectively forces paint and coatings producers (and the users of paints and coatings) to reduce the use of paint formulations that emit the volatile organic compounds (VOCs), to reduce certain chlorinated solvents in paint formulations, and places limits on the use of many paint formulating materials that are considered to be hazardous air pollutants (HAPs). Furthermore, there is a push to reduce chromate pigmented coatings that are the best agents for corrosion inhibition on aluminum. Chromate pigments contain hexavalent chromium, a health hazard that is increasingly regulated. Of the currently available liquid based paints and coatings, 95% contain VOCs, HAPs, or chlorinated solvents and will therefore will be affected by the CAA regulations. Not only can reformulation increase the cost of the coating materials to DoD organizations, but the new coating formulations may be less effective. Therefore, there is a need for the development of advanced coatings for DoD

applications that have lower VOC emissions, eliminate the use of chromate conversion coatings, and possess longer effective coating lifetimes.

To address the need for new environmentally compliant high performance coatings, TDA Research, Inc. (TDA) has proposed the development of a new class of high performance coating materials based on molecular composites known as carboxylato-alumoxanes. These materials consist of a boehmite particle covalent bound within a organic periphery. Functionalization of the organic groups allows incorporation of the boehmite particles into standard coating materials such as epoxies and urethanes. The presence of the bound boehmite platelets in the coatings is expected to drastically reduce diffusion rates through the films. Similar effects have been previously observed for flake or leafing pigments such as mica. Thus, the boehmite containing coatings act as barrier coatings to help prevent corrosion. However, we are not depending solely on barrier effects to minimize or prevent corrosion; we will also evaluate carboxylato-alumoxanes that contain active inhibitors covalent bound to the boehmite particles. Once class of inhibitors are phosphates which can stop corrosion by forming insoluble "noble" inorganic phosphates. We will also evaluate organic substituents based on phenol/quinone couples. Previous work has shown that tannins (i.e. polyphenols) are active corrosion inhibitors.

The research and development project will be carried out by TDA (Dr. Ronald L. Cook), Rice University (Professor Andrew Barron) , and University of Missouri-Rolla (Professors James O. Stoffer and Professor Harlan Anderson). The research effort will focus on the development of two classes of carboxylato-alumoxane coating materials. The first class of materials will be carboxylato-alumoxanes based on the use of hydroxybenzoic acids. From these carboxylato-alumoxanes we will prepare alumoxane based phenolic and epoxy coupling layers on the metal surface. The alumoxane-phenolic and alumoxane-epoxy coupling layers will provide very strongly bonded coatings with good mechanical properties and high corrosion resistance. The coupling layer will also provide a base coating for the attachment of the carboxylato-alumoxane topcoat. The topcoat will be prepared using alumoxane-urethane or alumoxane-acrylic materials that can be cross-linked with the coupling layer to form stable corrosion/erosion resistant high performance coatings. The successful development of these carboxylato-alumoxane materials will result in the development of composite coatings with low VOC emissions and high corrosion resistance without the use of chromate conversion coatings.

2. Background

2.1. Corrosion Control and Protective Coatings

It has been estimated that the total cost of corrosion to the United States economy may be as much as 4% of the gross national product. Maintenance costs associated with paint stripping and repainting alone costs the U.S. Air Force $700 million per year. The corrosion of airplanes and naval vessels is of particular concern to Department of Defense Forces since their equipment must be mission ready and operate under a range of severe conditions. Corrosion related equipment downtime presents a significant challenge to mission readiness in military operations and leads to increased operational costs.

The greatest contribution to the control of corrosion has been the widespread use of protective organic and mixed organic/inorganic coatings. Such coatings protect more metal on a tonnage

basis than any other means of corrosion protection. Unfortunately, the Clean Air Act (CAA) of 1990 will require paint and coating producers to significantly modify paint and coating formulations that have worked well for years. The legislation effectively forces paint and coating producers to reduce the use of solvents that emit the volatile organic compounds (VOCs), which are the precursors to the formation of smog. The CAA will also limit the use of certain chlorinated solvents which are implicated in the destruction of the ozone layer. In addition, it also limits the use of paint formulating materials, which are considered hazardous air pollutants (HAPs). The new CAA regulations go into effect in 1997 and 1998 for architectural, industrial maintenance, automotive, wood furniture, and aerospace coatings. Chromate pigmented coatings are currently the best agents for corrosion inhibition on aluminum and are therefore an important product in the aerospace coatings industry. Other environmental regulations limit the use of heavy metal pigmented paints and coatings, such as chromates, that are considered human health hazards. While chromate replacements are available, they have only 80% of the corrosion resistance of coatings that contain chromate pigments (Reisch, 1995).

Of the currently available liquid based paints and coatings, 95% contain VOCs, HAPs, or chlorinated solvents and will therefore will be affected by the CAA regulations. To meet the regulatory requirements, current paint and coating formulations will have to be significantly reformulated or new coating materials will have to be developed. Reformulation of paints and coatings in order to come into environmental compliance is expected to be costly and additional reformulation steps may be needed if the regulations become stricter (either at the federal or state (e.g. California) levels).

Organic coatings (latex paints, epoxy based coatings, etc.) are lightweight, provide corrosion resistance, and can be applied to a range of materials. Unfortunately, organic based coating formulations have a number of limitations. Except for some fluorocarbon and aromatic materials, most organic coatings cannot be heated above 150°C without melting or decomposing. Also, organic polymer based coatings will swell or dissolve in hot organic solvents, lubricating oils or hydraulic fluids, and few organic coatings are stable for long term ultraviolet exposure. As a result increasing numbers of polymer and coatings chemists therefore have been exploring the use of composite and hybrid coatings.

Organic polymers, along with metals and ceramics, are the three main classes of engineered materials. Each of these groups of materials possesses advantages and disadvantages not shared by the other two groups. Composite and hybrid coatings can potentially combine the advantages of two or three of these groups of materials while minimizing the disadvantages. An approach to the design of corrosion and erosion resistant coatings is the development of molecular scale hybrids that possess the properties of both polymers and ceramics. The organic components of the macromolecule could provide solubility, processability and flexibility to the material, while the ceramic component could provide hardness, heat resistance, UV stability, etc. Although research is advancing on towards the development of hybrid organic-ceramic materials (e.g. sol-gel materials incorporating organic groups and organic intercalated clays), these materials have a number of disadvantages including complex processing requirements, instability and high costs. One class of materials being developed at TDA and Rice University that can be used to design hybrid coatings is carboxylato-alumoxanes. These materials are molecular scale hybrid materials that are easy to prepare from low cost reagents, and that can be incorporated into advanced coatings by taking advantage of functional groups that can be built into the carboxylato-alumoxane structure.

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2.2. Low VOC Coatings Research

As a result of the regulations of the Clean Air Act of 1990, and other regulations that restrict the release of hexavalent chromium into the environment, there has been a significant push by the coatings industry to develop low-VOC emission coatings and surface treatments that can eliminate the use of chromate conversion coatings. At the same time, the coatings industry is trying to reduce the costs of current formulations and technologies and to improve the coating stability towards environmental factors and mechanical wear.

The coating and paints industry has been able to lower VOCs by using several approaches including:

- Prepolymer solutions: these materials are reduced viscosity solutions of low molecular weight polymer(s) that can form thermoset or thermoplastic coatings during the curing process.

- Powder coatings: these coatings are based on the use of fine particulate dispersions of powdered multifunctional monomers, used in the absence of a solvent.

- Water-born systems: these systems contain water-insoluble polymers in an aqueous suspension, stabilized with dispersants and surfactants.

- Reactive diluents: in this approach both the solvent and the monomers react during polymerization, thereby becoming an integral part of the polymer film instead of a VOC component.

All of these approaches have met with some success and have allowed reduction of VOC to near or below mandated VOC levels. TDA's project will take advantage of these advances when formulating the carboxylato-alumoxane coatings.

2.3. Chromate-Free Corrosion Coatings

The efforts by the coatings industry to identify chromate-free corrosion coatings have been less successful than efforts to develop low-VOC coatings. Although many approaches have been evaluated, to date they have generally offered less corrosion protection than chromate based coatings. The approaches being considered to replace chromate conversion coatings are too numerous to present in detail here but include: the use of MO_4^{n-} analogs of chromate such as molybdate (MoO_4^{2-}, MnO_4^{2-}, WO_4^{2-}, etc.), modified phosphate treatments, modified anodic coatings, anodic spark deposition, rare earth additives such as Ce(III), pyrolytic tin oxide, ion beam and physical vapor deposition coatings, and organic, organometallic, polymer and sol-gel derived coatings. A more detailed overview of the work being carried out in this area has been presented by Cohen (1995). Research in the above areas is ongoing, and no clear winners have yet emerged.

2.4. Carboxylato-Alumoxanes

Carboxylato-alumoxanes are low cost nanocomposite materials prepared from the reaction of carboxylic acids and the mineral boehmite $((AlO(OH))_2$, ~$1/lb). Carboxylato-alumoxanes are ~50 -100 nm boehmite particles whose surfaces are covered with covalently attached carboxylic acids (Figure 1). The properties, and processability of the carboxylato-alumoxanes are strongly dependent on the nature and size of the organic group attached to the boehmite core. The chemical reactivities of the carboxylato-alumoxanes are dependent on the functional groups attached to the boehmite particle through the carboxylic acid.
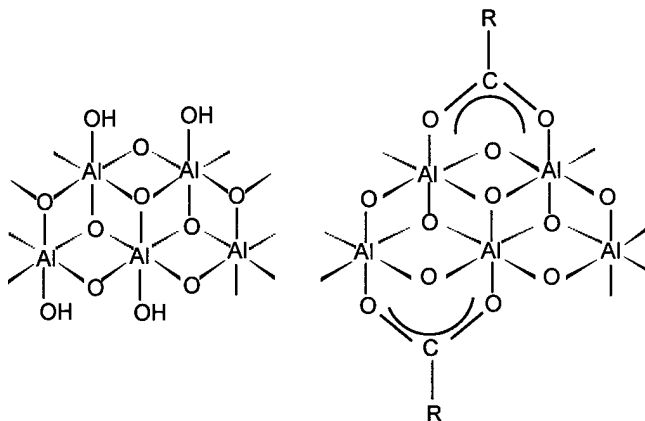
Figure 1. Comparison of the core structures of boehmite and the carboxylato-alumoxane

The usefulness of alumoxanes as molecular composites for advanced coating materials and for other applications has been limited because the initial synthetic methods were difficult and used expensive precursors. Until recently, alumoxanes were prepared from pyrophoric organo-aluminum compounds such as triethyl-aluminum. For example, carboxylato-alumoxanes were prepared by the reaction of triethylaluminum with carboxylic acids followed by hydrolysis of the reaction mixture (Pasynkiewicz 1990). Recent work by TDA and Professor Barron's group (Rice University, Landry et al. 1995) has shown that a wide range of carboxylato-alumoxanes can be prepared by the reaction of boehmite and a carboxylic acids in an appropriate solvent. TDA and Professor Barron's group have prepared a range of alumoxanes possessing solubility in both organic solvents and in water. In addition, TDA and Professor Barron's group have prepared carboxylato-alumoxanes containing functional groups (e.g. -OH, -NH$_2$, Br, etc.) that allow standard polymer chemistry to be carried out on the carboxylic acids attached to the surface of the boehmite particles. Since thousands of carboxylic acids containing a wide range of functional groups are available, the properties (e.g. hardness, U.V. stability, corrosion resistance, surface adhesion, etc.) of carboxylato-alumoxanes coatings can be tailored for a specific application. Additionally, several carboxylic acids can be attached to the boehmite core simultaneously to introduce multiple functional groups for subsequent reactions

As synthesized, the core of the carboxylato-alumoxane particle consists of boehmite, an aluminum oxy-hydroxide of the composition $(AlO(OH))_n$. However, TDA and Professor Barron's group have recently developed a synthetic route for introduction of a wide range of cations into the boehmite lattice at room temperature. The identification of this synthetic route provides a means to vary the properties of the boehmite core as well as the organic periphery. This will allow us to introduce color (e.g. blue using cobalt cations, green using nickel cations, etc.) into the alumoxane based coatings without the addition of organics that add little to the structural and mechanical integrity of the coatings.

The metal exchange reaction is accomplished by the reaction of metal acetylacetonates $(([CH_3C(O)CHC(O)CH_3]^-)_n M^{n+})$ with the carboxylate-alumoxane. ^{27}Al NMR studies carried out by

Professor Barrons group have shown that aluminum cations (Al^{3+}) are extracted from the lattice as $Al(acac)_3$ and replaced by the metal-acetylacetonate cations. Since this process leaves the organic core undisturbed, the desirable properties imbued to the carboxylato-alumoxanes by the organic groups are retained.

3. Technical Approach

The goal of this ARPA/ONR funded research and development project is the development of advanced corrosion/erosion resistant coatings that can meet three criteria: prevention of corrosion of aerospace aluminum materials without the use of chromate inhibitors, low VOC emissions from the formulated coatings, and extended life of the coatings to meet the timelines of Programmed Depot Maintenance time schedules. We expect that these goals can be met by the use of two closely-related carboxylato-alumoxane coating formulations. A thin, carboxylato-alumoxane coating will be developed that can chemically bond to the metal surface, and thereby eliminating the need for chromate conversion coatings and primers.
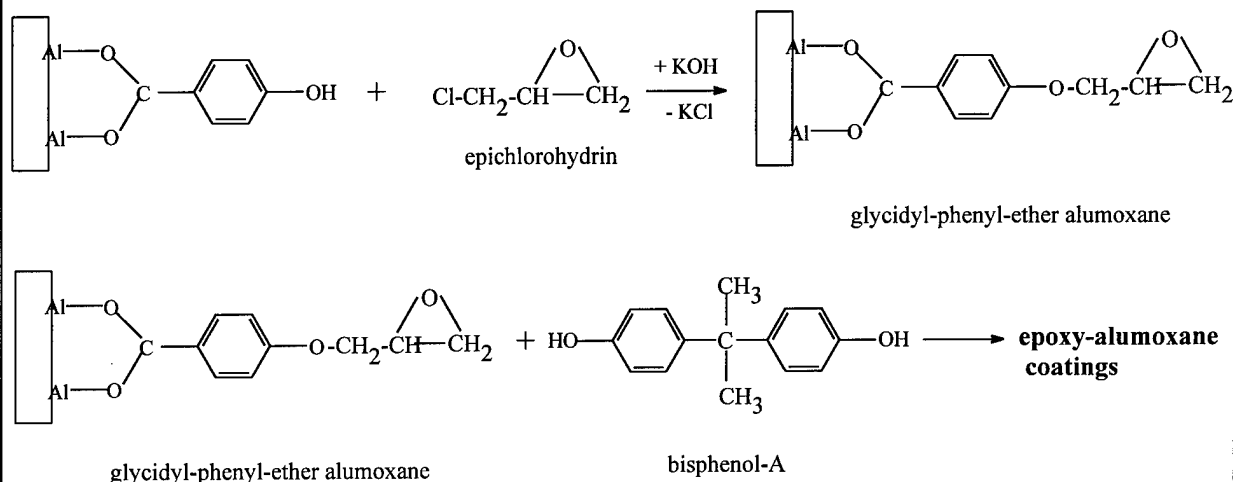
The carboxylato-alumoxane "primer" layer provides three functions. As a passive coating, the carboxylato-alumoxane layer provides a strongly-bound, chemically-resistant barrier coating to water and oxygen to protect against corrosion. The carboxylato-alumoxane primer will also contain active corrosion inhibitors in the form of phosphorus groups and phenol/quinone groups to prevent corrosion. The carboxylato-alumoxanes can be incorporated into current coating systems to improve their properties in a variety of ways. The systems under consideration include epoxy resins, urethanes and acrylics. Figure 2 shows simplified reaction schemes that are being used prepare the desired alumoxane-epoxy-resin, and alumoxane-urethane-resin coatings. The rationales for the use of these materials in the coatings are given below.

Epoxies are large class of thermoset resins that are being used as protective coatings. Their preparation does not require high temperatures, are exothermic (70-80 kJ/epoxy equivalent), and their curing can be readily catalyzed. They stand on their own as coatings when combined with Bisphenol A, or can be exploited as curing agents for other polymeric systems. Their cross-linking ability allows them to make a significant contribution to the emerging "zero VOC" powder coatings industry. The versatility of epoxies is demonstrated by their reactivity to a variety of functional groups, including carboxylic acids and anhydrides to form polyesters, alcohols to form chemically resistant ethers, and primary amines to form oxazolidines, currently under investigation for low VOC coatings. The flexibility of epoxies is also demonstrated by their use with isocyanates, silicones and amides, both as monomeric systems or in pre-prepared polymeric frameworks. The outstanding properties of epoxies are a result of stable C-C bonds and ether linkages that provide chemical resistance, hydroxyl groups that assist in adhesion, and aromatic rings that enhance thermal stability.

We expect that composite alumoxane-epoxy coatings would exhibit the favorable properties of both the epoxies and alumoxanes. However, outdoor weathering of epoxy coatings has been observed to lead to cracking of the coating. Thus epoxy resins are most commonly used for primers and undercoats, where adhesion and corrosion resistance are particularly valuable. The desirable chemical properties of epoxy based coatings are somewhat offset by their susceptibility to weathering, we will therefore use alumoxane-urethane resins as topcoats.

Synthesis of Alumoxane-Epoxy-Coat Precursors

epichlorohydrin

glycidyl-phenyl-ether alumoxane

glycidyl-phenyl-ether alumoxane   bisphenol-A   epoxy-alumoxane coatings

Synthesis of Alumoxane-Urethane-Coat Precursors

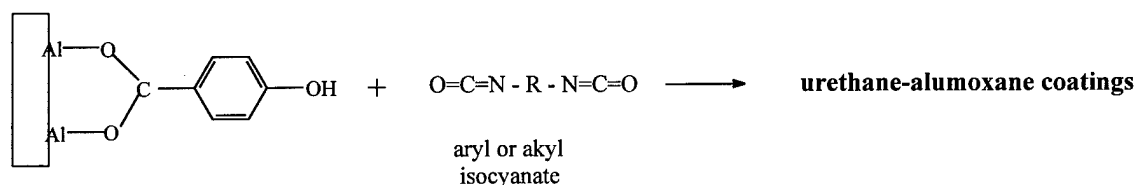aryl or akyl isocyanate   urethane-alumoxane coatings

Figure 2. Reaction schemes for preparation of alumoxane based composite coatings

Urethanes are perhaps the most versatile of all coating formulations. Like epoxies, they react with alcohols, amines and carboxylic acids at room temperature and have excellent adhesion properties. Multifunctional isocyanates are inexpensive to prepare and are quite versatile in the properties of the resulting film. Isocyanate cured polyesters are used in paints and topcoats because of their excellent weatherability and chemical resistance. We anticipate that incorporation of alumoxanes into the urethane framework will lead to the development of alumoxane-urethane composites with improved scratch and impact resistance. Acrylics also provide tough, abrasion resistant coatings, and along with polyesters, make up a large segment of the coatings market. They are generally cross-linked with epoxies and isocyanates as part of a two component system. Alumoxanes can be easily incorporated into the acrylic polyol and polyester component of the coatings formulation.

4. Research Results September 19th- December 19th 1996

4.1. Research Progress

This quarters report is divided into three sections. The first section contains the results of our efforts to synthesize the carboxylato-alumoxanes precursors and their conversion to coating materials. The second section describes coatings efforts that have just begun using the alumoxane materials, and the third section outlines the characterization efforts that are being

developed to characterize the coatings and the measurements that will be carried out to characterize the corrosion control offered by the alumoxane-resin coatings.

Syntheses of Carboxylato-Alumoxanes and Alumoxane Resin Coating Materials

The approach TDA has taken for the preparation of new corrosion and erosion resistant coatings is based on the use of carboxylato-alumoxanes. We are preparing alumoxane materials that will reduce corrosion through their barrier properties. We are also preparing alumoxane materials that will perform as active corrosion inhibitors. In these latter materials, we are incorporating both phosphorus and phenol/quinone reactive groups. As discussed in the background section, carboxylato-alumoxanes are a new class of materials that are prepared by the reaction of carboxylic acids with pseudoboehmite or boehmite particles in an appropriate solvent. Since many of the carboxylato-alumoxane materials and their functionalized derivatives have not been prepared before, our first two quarters efforts have been primarily directed towards the synthesis of functionalized alumoxanes (e.g. alumoxane epoxies, urethanes, etc.) that can be converted into the desired coatings.

<u>Synthesis of Carboxylato-Alumoxane Monomers</u>

In our previous monthly we provided detailed synthesis of several carboxylato-alumoxanes that were used as precursors for the preparation of alumoxane resins that could be used as new coating materials. The carboxylato-alumoxane materials synthesized during the first quarter's efforts are based on the use of hydroxybenzoic acids. Use of this particular carboxylic provided a direct route to the synthesis of the glycidyl-phenyl-ether (GPE) alumoxanes (Figure 3) that we have used to prepare alumoxane epoxy coatings. In order to generate a database from which
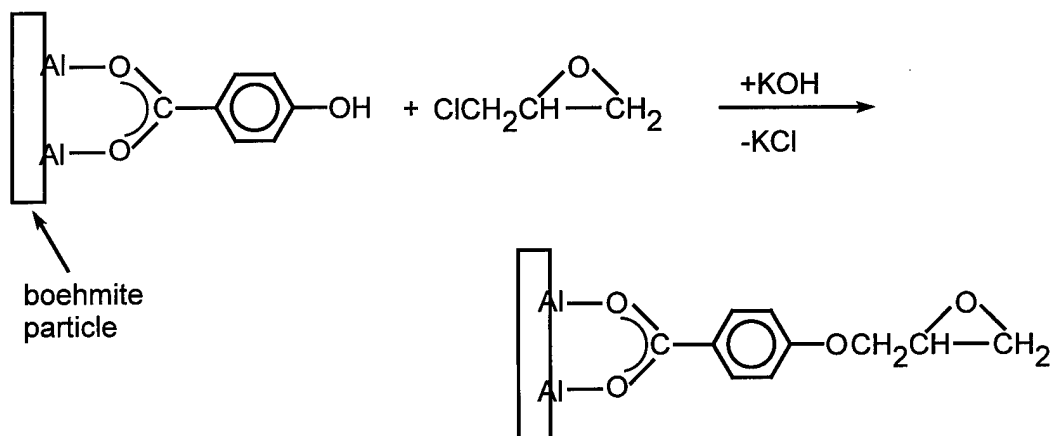

Figure 3. Synthesis of the GPE-alumoxane from hydroxybenzenato-alumoxane

the properties of the epoxy coatings can be related back to the alumoxane precursors we have prepared several additional carboxylato-alumoxanes that can be converted to alumoxane epoxies. As one new alumoxane-epoxy precursor we have prepared a new alumoxane by the reaction of boehmite with diphenolic acid, or 4,4-bis-(4-hydroxyphenyl) valeric acid (Figure 5). This carboxylic acid has two phenolic groups attached to an aliphatic backbone. We anticipate that the presence of the aliphatic chain may allow the alumoxane-epoxy coatings incorporating this precursor to be more flexible (and perhaps more processable). We have also prepared an alumoxane precursor that can be used to prepare an alumoxane-epoxy coating that does not

contain aromatic functional groups (and should therefore be UV stable). This carboxylato-alumoxane precursor was prepared by the reaction of boehmite with dimethylol propionic acid (Figure 4). The syntheses of these two alumoxanes are described detail below.
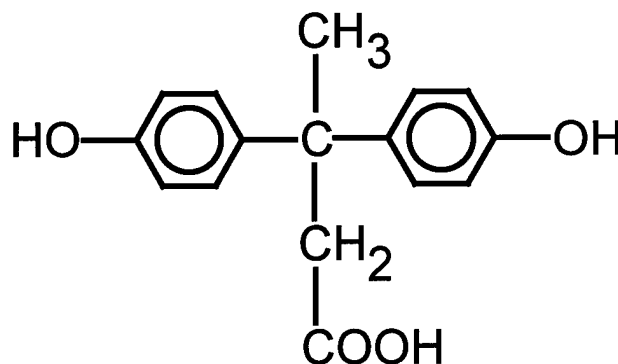
Diphenolic acid is reported to be soluble in acetone, methyl ethyl ketone, ethanol, isopropyl alcohol, acetic acid and hot water. A solubility test indicated that diphenolic acid, (DPA), was soluble in warm methyl ethyl ketone, (MEK), dilute acetic acid, but insoluble in hot water or xylene. The alumoxane product is expected to have similar solubility

Figure 5. Structure of diphenolic acid

properties as Bisphenol B, $CH_3C(PhOH)_2(C_2H_5)$(a common phenolic used in the preparation of epoxy resins). These include good solubility in acetone (266g/100g solvent), methanol (166g/100g solvent) and benzene (2.3g/100g solvent). The first two are also good solvents for DPA, but benzene and presumably xylene may be good solvents to separate the DPA from the alumoxane. A two solvent system of MEK/xylene was thus chosen as the reaction medium. DPA (14.3g, 0.05 mol) was added to 50 ml of MEK and heated until all of the acid was dissolved. Xylene (50ml) was then added slowly to avoid the precipitation of the phenolic acid. While stirring, 2.9g Catapal B was added, and the system was refluxed for three days at 90°C. A white powder was then filtered from the hot solution. The lower boiling point MEK solvent was slowly evaporated off, resulting in a trace of pink precipitate that was identified by FTIR as DPA. The filtered solid was washed with cold acetic acid, water and then dried. This material was then characterized using FTIR, and TGA.

The FTIR spectrum of diphenolic acid and the alumoxane product is shown in Figure 6. DPA has an absorption at 1708cm^{-1} typical of a free carboxyl group, along with the phenolic ring stretch at 1556 cm^{-1}, 1496 cm^{-1} and 1475 cm^{-1}, while alumoxane product shows a shift in the carbonyl absorption from 1708 cm^{-1} to 1610 cm^{-1}, indicating the formation of a carboxylato- alumoxane. A strong peak is also
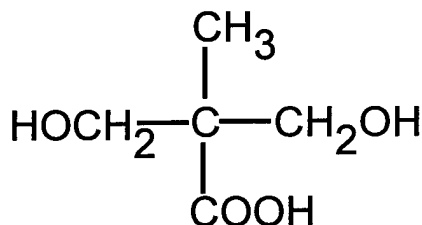
Figure 4. Structure of dimethylol propionic acid.

observed at 1190 cm^{-1}, and that is generally associated with an ester or ether C-O stretch. The thermal-oxidative behaviour of the DPA-alumoxane is similar to that observed for other alumoxanes prepared by TDA and Rice University. Small losses of water are observed at temperatures above 100°C. Starting around 300°C in air the DPA-alumoxane begins to decompose resulting in the formation of gamma-alumina as the only solid product remaining at 600°C.

We have also prepared a carboxylato-alumoxane from dimethylol propionic acid (DMPA) and boehmite. This organic acid was chosen to prepare a new carboxylato-alumoxane because epoxies that are free of aromatics are more stable towards UV irradiation. Aromatic containing epoxies are known to yellow under UV exposure. The DMPA-alumoxane will be used to prepare both urethane and epoxy resins. DMPA (67g, 0.5mol) was dissolved in 200 ml of water. With stirring, Catapal B (29.4g, 0.5mol) was added to the mixture and the mixture refluxed for three days. The water was removed under vacuum and the remaining solid was
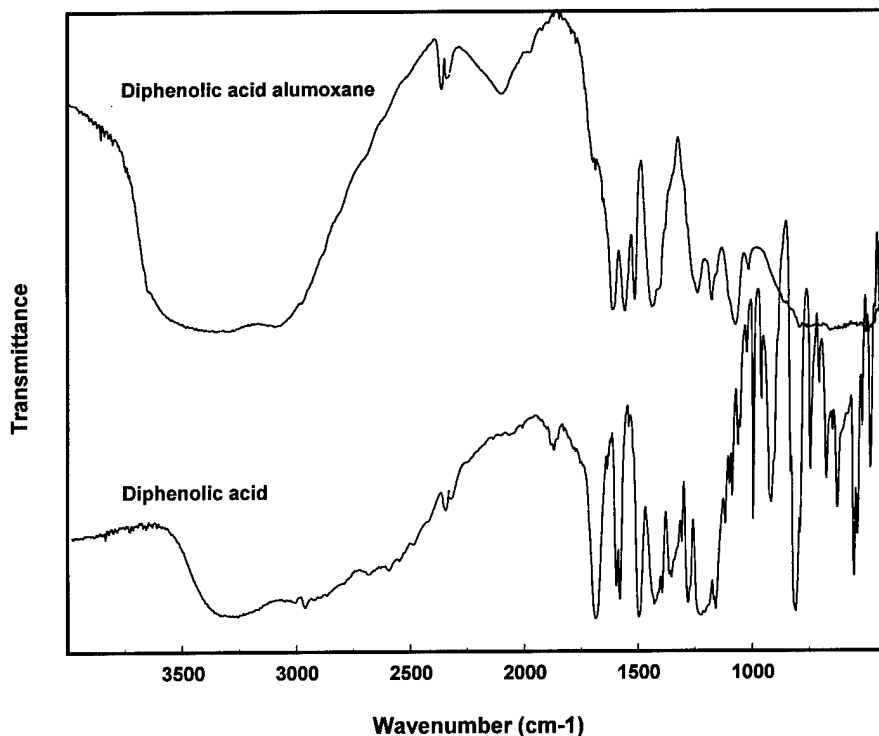
Figure 6. FTIR of DPA and DPA-alumoxane

washed with warm ethanol. The ethanol soluble fraction was allowed to dry, leaving a white powder identified by FTIR as DMPA. The fraction that was not soluble in ethanol was also examined by FTIR and shown to be the DMPA-alumoxane. XRD and TGA characterizations of the DMPA-alumoxane material are currently being carried out. We are also in the process of converting both the DPA-alumoxane and the DMPA-alumoxane to the epoxy precursors.

Synthesis of Phosphorous-Containing Carboxylato-Alumoxanes

We have begun to prepare and characterize carboxylato-alumoxanes containing phosphorus groups. Incorporation of phosphorus into the carboxylato-alumoxanes has then potential to modify the coating properties of the alumoxanes in several ways. Previous work by Professor Barron's group has observed that pure phospho-alumoxanes tend to cold flow. We may be able to take advantage of this property to "self-heal" scratches in the alumoxane coatings. Addition of phosphorus groups to the alumoxanes appears make the resulting alumoxanes significantly harder. Phosphorus containing materials are also known to be active corrosion inhibitors. Therefore, we are also considering using the phosphorus containing alumoxanes as reagents for "phosphating" treatments of the aluminum surface to provide a hard organic-inorganic coating on the aluminum surface. The P(O)OH group in compounds such as $(CH_3O)_2P(O)OH$ is iso-structural with the C(O)OH group in carboxylic acids. The oxygen-oxygen distances are also close to those in the carboxylic acids. It was therefore anticipated that phosphonate groups could be incorporated into the carboxylato-alumoxane structure. The results of the incorporation of a dimethylphosphinate group into a acetato-alumoxane are given below.

Synthesis of acetato-phosphonato-alumoxanes (APA)

A sample of acetato-alumoxane AA (8.37 g) was dissolved in H_2O (90 ml), and then $HO(O)P(OMe)_2$ (3.25 g) was added to the mixture. The reaction mixture was refluxed for 2 h., after which the solution changed from clear (colorless) to cloudy white. Removal of the solvent under vacuum, followed by washing with MeOH gave a white solid which was dried at 90 °C under vacuum. Yield *ca.* 10g. The sample was redissolved in H_2O and left in a mold to dry overnight. The ceramic yield of the APA (75.9 %) is similar to the AA (75.1 %), but the thermal properties (as determined by TGA/DTA) are drastically different. The TGA analysis of the APA as compared to the parent AA indicates that the presence of the phosphinate increased the thermal stability with respect to decomposition below 150°C (302°F). However, the final decomposition point remained unchanged (*ca.* 500 °C). The IR spectra of the APA indicates bands (1180 - 1200 cm^{-1}) that may be assigned to $Al[\mu\text{-}O_2P(OMe)_2]Al$ units, and a band at 1050 cm-1 that is characteristic of a P-O-alkyl stretch. The ^1H NMR shows multiple peaks due to both the acetate and phosphinate (3.7 - 3.4 ppm) groups. While the ^{31}P NMR shows a broad peak at 3.65 ppm, characteristic of the phosphinate. These results indicate that the phosphinate groups can be successfully incorporated into the carboxylato-alumoxane structure. Hardness measurements have shown that the hardness of APA as measured by microindentation (860 Kg/mm^2) is an order of magnitude higher than that of AA (90 Kg/mm^2). This is significant since on the mohs scale APA (6-7) is actually comparable to human teeth (7), whereas AA (3.5 - 4) is comparable to PMMA, and other organic polymers. Therefore, it may be possible to prepare erosion resistant coatings with hardnesses approaching on those achieved by HVOF or plasma spraying with the carboxylato-phosphonato-alumoxanes. Particle size measurements suggest that there is little change in particle size upon formation of APA from AA. We will continue efforts in this direction to determine if the carboxylato-phosphonato-alumoxanes can be used to prepare hard corrosion resistant coatings on aluminum substrates.

Incorporation of Epoxy Groups into Carboxylato-Alumoxanes Using Epichlorohydrin

During the second quarter of this project we have begun to incorporate epoxy functional groups into the carboxylato-alumoxane structure by reaction of the alumoxane with epichlorohydrin (see Figure 3). In our initial efforts we converted the hydroxybenzenato-alumoxane to the glycidyl-phenyl-ether alumoxane. The details of the experimental approach are given below.

A mixture of epichlorohydrin (ECH), 4-hydroxybenzenato-alumoxane (4-HBA), and KOH are added to a mixed solvent of 20 ml water + 100 ml Xylenes. The ratios of the reactants were 10:1 ECH to 4-HBA, 2:3 KOH to ECH (10g (0.025 equiv. of OH based on TGA) of 4-HBA + 46g (.50 mol) ECH + 18.5g (0.33 mol) KOH). The synthetic approach for introducing the epoxy group into the 4-HBA structure followed a standard procedure for synthesis of organic epoxies with epichlorohydrin (Potter 1970). The water and some of the ECH are removed by distillation. 1-2 ml of the water (the water wt% needs to be between 0.5-3.0 wt% of reaction mixture) and all of the ECH is returned to reaction mixture and mixture is heated to reflux for 2-3 hours. (A solvent recovery distillation head was used both to collect the water and ECH and return most of the ECH and a small amount of water back to the reaction flask). The unreacted ECH and most (70-80%) of xylenes were then removed by distillation. The mixture was then filtered to remove any solid material and the remaining xylenes removed under vacuum yielding

he glycidyl-phenyl-ether (GPE) alumoxane as a viscous liquid. The GPE-alumoxane can then be reacted with 4-HBA or 4-aminobenzenato-alumxoane (4-ABA) and a catalyst to prepare the alumoxane containing epoxy resins for coating the aluminum substrates. The syntheses of the alumoxane-epoxy resins are described in the next section.

Synthesis of Alumoxane-Resins from Carboxylato-Alumoxane Monomers

In this section we describe the syntheses of alumoxane resins using the carboxylato-alumoxane precursors. The alumoxane-epoxy resins along with the alumoxane-urethane-resins form the basis of our proposed coating approach.

Synthesis of Alumoxane-Epoxy Resins - The first alumoxane-epoxy-resin that we have prepared is based on the reaction of a GPE-alumoxane with 4-HBA. This reaction is catalyzed by small amount of base (1-methylimidazol upon heating to 140°C-170°C. An (approximately 25% cross-linked) epoxy resin was prepared from 2 grams of the GPE-alumoxane(8.0 mequiv. Epoxy groups) with 0.4 g 4-HBA (2.0 mequiv Hydroxy groups) + 0.026 g of methylimidazol. The resin and 4-HBA are mixed and then the 1-methylimidazol is thoroughly mixed into the resin. The mixture was then heated at 1C/min to 140°C for 2 hours. The material was still tacky so temp was ramped to 150C and held for 2 hours. The material was still tacky so temp was ramped to 160C and held for 2 hours. The material was still tacky so temp was ramped to 170C and held for 2 hours. At this time the material became set and was no longer tacky. A hard tough alumoxane resin material resulted from the cure process.

Synthesis of Alumoxane-Containing DOW DER 332 DGEBPE Resins - Another route to the development of corrosion/erosion resistant coatings is incorporation of alumoxanes into commercial epoxy resins. To demonstrate that this could be achieved we carried out an evaluation of the reaction between 4-HBA and DOW DER 332 DGEBPE epoxy resin. The DOW resin (3g) was heated to 40°C and 4-HBA (2g) was added and the two components we thoroughly mixed. Then 0.025g of 1-mehtylimidazol was added to the mixture as a catalyst. The sample was maintained at a temperature between 35°C-45°C during this process. The mixture was then coated onto an aluminum substrate and heated to 140°C for at least 6 hours. The material cures to a hard coating that can be sanded. The cured alumoxane-containing DOW resin is not scratched by copper or nickel coins and is only slightly scratched by a hardened steel knife edge. The FTIR of the alumoxane containing DOW resin is shown in. Our calculations (based on the equivalents of -OH groups on the and equivalents of epoxy groups in the DOW resin) suggested that we would not achieve full cross linking of the epoxy resin. The FTIR is consistent with this calculation and shows the presence of the methylene groups of the epoxy group (in the 2900-2700 cm^{-1} region) in the cured resin.

Coatings Work Performed At University of Missouri-Rolla (UMR)

As part of this DARPA funded project to develop corrosion/erosion resistant coatings for aluminum substrates, Professor Stoffer and Professor Anderson have several roles at UMR. One role is the development of suitable formulation and application methods for applying the alumoxane based coatings to the aluminum substrates. Another role is to identify possible non-chromate surface conversion treatments that may lead to enhanced corrosion protection of the aluminum substrates. Alumoxanes synthesized by TDA and Rice University are being sent to UMR where formulations and application methods are being developed. Characterization of the mechanical properties and corrosion/erosion resistance afforded by the films are then

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communicated TDA/Rice University, who then modify the alumoxanes to improve the coatings. The performance of the alumoxane coatings are being evaluated by a series of tests normally performed on industrial coatings. For the alumoxane coatings Professor Stoffer has divided the UMR work into several tasks. These include;

- Substrate preparation
  - Deoxidized and/or phosphate treated aluminum

- Conversion coatings
  - UMR applying Alumoxane as a conversion coating
  - UMR's cerium conversion coatings
  - UMR's ceramic polymer coating (Anderson method)
  - UMR's plasma sprayed ceramic coating with Alumoxane

- Paint formulation
  - Alumoxanes as corrosion inhibiting coating in a classical organic coating
  - Alumoxanes as soluble materials in a water reducible coating (epoxy, acrylic, etc.)
  - Classical corrosion inhibitors as comparison materials (Busan, Molywhite, etc.)

- Application methods
  - Spraying, roll coating, brushing etc.

and

- Testing of the coated aluminum substrates by standard ASTM methods
  - Adhesion, cross hatch tape test
  - Adhesion, cloth peel test if cross hatch not differentiate coatings
  - Abrasion, Tabor or falling sand method
  - Hardness, pencil test, Moh hardness
  - Corrosion tests, salt fog test, Prohesion tests, scribed and unscribed
  - Flexibility, Mandril bend SEM, ESCA, Auger characterization of substrate, conversion coatings and films

The experimental efforts that are being carried out under these tasks are described below.

The formulation of several epoxy coatings with the water soluble 4-hydroxybenzenato-alumoxane precursors was evaluated by UMR. Here commercial formulations were evaluated where the p-hydroxybenzenato-alumoxane provides the -OH functionality for cross-linking Initial use of the 4-HBA material in the formulation resulted in solidification during preparation or separation into a nonhomogeneous system. This is what usually happens with the first attempts with formulations involving new materials. A series of additives are being used to gain stability using the 4-HBA component. As a readily available substitute for the alumoxane, talc is being used to assist the formulation process and determine the proper ratios of the non-alumoxane components in the formulation. Using talc UMR has developed a formulation that works. This formulation is now being evaluated for use with the alumoxanes If the formulation

formula is successful then the coatings will be applied to the aluminum substrates for testing and evaluation.

UMR is also evaluating several possible conversion coatings onto which the alumoxane coatings will be applied and as reference coatings to compare with the alumoxanes. In initial experiments, CeO_2 and $Y-ZrO_2$ thin films were spin coated onto one inch by one inch aluminum substrates. Aluminum substrates were degreased, deoxidized and stored in distilled H_2O prior to use. Prior to coating by the ceramic precursor, the substrates were spun dry at 4000 rpm. The ceramic precursors appeared readily wet the aluminum substrates after the deoxidizing procedure. After each spin coating, conducted at 4000 rpm, samples of both CeO_2 and $Y-ZrO_2$ were held at either 150°C or 300°C for 30 minutes. This procedure was repeated until 3 coatings had been applied. All the films appeared homogenous, except where touched by the forceps when removing from the distilled H20 bath.

UMR is also evaluating the possibility of using plasma spray coating methods to apply a dense adherent boehmite coating to the aluminum substrates. Plasma spray technology will be used to apply these films to 7075-T6 aluminum coupons. Processing parameters will be explored that maintain the coupon temperature below 150°C to limit further aging of the aluminum substrate. Microhardness tests will be used to monitor changes in mechanical properties of the substrate.

To maintain the low substrate temperature the alumoxane precursors will be directly fed into the plasma stream as a liquid suspension. The ideal candidate liquid would be a polar molecule that would wet the powders to break-up the agglomerates and then decompose to a gas in the electric arc to help disperse the powders and maintain a low substrate temperature. Water would be an interesting, if not ideal, candidate since decomposition products, if present, would promote the formation of the hydroxide end groups. Slurries will be delivered using an auger arrangement that would force the slurry through a tube into the gun and finally into the plasma stream. Other advantages to injecting the plasma stream with a liquid suspension would be to regulate the melting and solidification of the nanocrystalline powders or to direct fire precursor gels in the plasma stream. It would be expected that the deposited coating would require a subsequent sintering operation to ensure full density of the boehmite surface layer. Here, we propose to use a laser to induce densification and sintering. Initial studies will examine post spray modification of the deposits followed by experiments where the laser is used simultaneously during the plasma spray deposition process. A plasma spray unit was recently acquired from the U.S.Bureau of Mines-Rolla Station (USBM). The unit is a 40 kW Plasmatron Spray System, manufactured by Miller Thermal Technologies, Inc. This unit has been moved to the Rolla campus, repaired, and installed in Fulton Hall. We have recently completed an environmental spray chamber that will provide for both a controlled atmosphere and operator safety in the operation of the plasma spray unit.

Film and Interface Characterization Studies (Rice University)

In addition to the synthetic efforts being carried out at Rice and TDA and the formulation and coating experiments being carried out at UMR we have mapped out characterization methods in order to fully characterize the films and the film interfaces. These efforts will be carried out by Professor Barron's group at Rice University.

Aluminum metal and alumoxane coatings.

The objective of this task is to characterize the mechanical and structural characteristics and chemical (oxidative/hydrolytic) stability of the interface between the aluminum substrate (or a conversion coating) and the alumoxane coating in order to optimize the processing conditions for subsequent coating fabrication. We will evaluate the effects of the surface pre-treatment, the alumoxane solution concentration (2 - 20 %), and the drying temperatures on the quality of the alumoxane coating. The coated aluminum substrates will be fractured and the coating examined using SEM imaging.

The alumoxane coating and aluminum-coating interface will be examined using a range of physical methods. The coated substrates will be analyzed by optical microscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and transmission electron microscopy (TEM) as appropriate to characterize the treatment product. Imaging and compositional analysis performed using a JEOL 5400 SEM and a CAMECA SX-50 Electron Microprobe will allow for observation of the uniformity of the alumoxane coating over the aluminum substrate. Cross-sectioned samples will be prepared using standard techniques and characterized by SEM, Electron Microprobe, and TEM (JEOL 2010). The analysis of samples in cross-section will specifically address the structure of the coating and interface as well as any chemical interaction. Infra-red (IR) spectroscopy (Nicolet Magna 760) will be used to analyze the bonding at the interface. The use of reflection IR will allow for the specific probing of both the modified aluminum surface and the interface between aluminum and the alumoxane. The results from this study will be analyzed in comparison with those of model aluminum compounds previously prepared in Professor Barron's laboratory.

Between alumoxane layers

The two primary methods for study of the interface between the alumoxane layers will be IR spectroscopy and solid state NMR spectroscopy (Bruker AM-200). The latter will employ particles rather than thin films, however, using CPMAS ^{13}C and T^1 measurements we propose to determine the extent and type of chemical bonding between different alumoxanes. In particular, the ability to form direct covalent linkages will be probed and compared with model systems.

5. References

Cohen, S.M., (1995). "Replacements for Chromium Pretreatments on Aluminum", *Corrosion*, **51**, 71.

Landry, C.C., Pappe, N. and Barron, A.R. (1995). "From Minerals to Materials: Synthesis of Alumoxanes from the Reaction of Boehmite with Carboxylic Acids", J.Mater.Chem., **59(2)**, 331.

Potter, W.G., (1970). "Epoxide Resins", Butterfield and Company Ltd.,London, Chapter 2.

Pasynkiewicz, S., (1990). "Alumoxanes: Synthesis, Structures, Complexes and Reactions", *Polyhedron*, **9(2/3)**, 429.

Reisch, M.S., (1995). "Paints and Coatings", *Chem.Engin. News*, Sept 25, 30.